

Influence of local structure on magnetic properties of Layered Cobaltites $\text{PrBaCo}_2\text{O}_{5+\delta}$, $\delta > 0.5$

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Abstract. The effect of local structure on the magnetic and transport properties of the layered perovskites has been investigated. The samples $\text{PrBaCo}_2\text{O}_{5+\delta}$, ($\delta = 0.80$ and 0.67) though crystallize in the same 112 type tetragonal structure have different magnetic ground states. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy has been employed to explain the changes in magnetic interactions based on the rotation and tilting of CoO polyhedra in these oxygen rich double perovskites.

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1. Introduction

Partial substitution of alkaline-earth metals for rare-earth metals in RCoO_3 (R - rare-earth element) and their subsequent ordering of results in double layered perovskites. One such Ba substituted layered perovskites are $\text{RBaCo}_2\text{O}_{5+\delta}$, ($0 \leq \delta \leq 1$). The ionic size difference between Ba and R and the resultant valance of Co due to oxygen non-stoichiometry make cobaltites more complex to study. They are of very special interest for their unique properties like metal insulator transition (MIT), spin state transition, charge ordering and giant magnetoresistance (MR)[1, 2, 3, 4, 5, 6, 7]. These properties have their origin in the strong interplay between crystallographic, magnetic and transport properties. A property that distinguishes the cobaltites from other transition metal perovskites is the crystal field splitting of the $3d$ energy level of the Co ion. It is of the same order of magnitude as the Hund's rule intra-atomic exchange energy. Spin state transition can therefore be easily provoked by varying temperature, pressure, magnetic field or chemical composition (oxygen content or rare earth ion) of the material. These spin state transitions are believed to be responsible for their unique properties. The transport properties of the layered cobaltites are found to be very sensitive due to the coexistence of ferromagnetic (FM) and antiferromagnetic (AFM) state. A giant negative magnetoresistance (MR) (of about 10%) coinciding with FM-AFM transition has been observed in $\text{GdBaCo}_2\text{O}_{5.5}$ [2]. Whereas $\text{LaBaCo}_2\text{O}_{5.5}$ exhibits a strongly irreversible MR near FM-AFM transition [8].

Oxygen non-stoichiometry is one of the important aspect in these layered cobaltites. Tailoring of oxygen content realizes in different valance states of cobalt ion ($2+$, $3+$, $4+$) and different local environments, both of which play a crucial role in their magnetic properties [9, 10, 11]. The structure of Co based double perovskites also depends on the oxygen content ($5 + \delta$). In general, the lower and higher oxygen content compounds crystallize in tetragonal structure with 112 type unit cell while the intermediate members crystallize in orthorhombic 122 type unit cell [10, 11]. The magnetic properties are found to be correlated to oxygen content and crystal structure. While the compounds with lower δ have AFM ground state, FM dominates in compounds richer in oxygen. When $\delta = 1$, the FM order is associated with metallic behavior due to double exchange interaction [12]. With the decrease in oxygen content, a transition from metallic to insulating state occurs in the paramagnetic state and further as the number of trivalent Co ions increase FM order changes to AFM ordering. Neutron diffraction studies on $\text{PrBaCo}_2\text{O}_{5.75}$ reveal a paramagnetic to FM and an incomplete FM to AFM transition[13]. Furthermore, in these oxygen rich compounds, the Co^{3+} ions in octahedral coordination are found to be in HS state as compared to LS state in $\text{PrBaCo}_2\text{O}_{5.5}$ [14]. It is therefore not clear if the HS to LS spin state transition of octahedral Co^{3+} ions is responsible for the transition from FM to AFM ground state. Or it is the delocalization of $pd\sigma$ holes that are responsible for the AFM to FM transition in these double perovskites [15]. Our recent studies have shown that local structure around Co ions plays an important role deciding the magnetic properties of these hole doped

cobaltites [16]. Hence it would be worthwhile to explore the local structure around Co ions in these layered cobaltites and correlate them with their magnetic properties. In particular, it would be interesting to examine the changes in local structure of Co ions as the ground changes from FM to AFM.

Extended X-ray absorption Fine Structure (EXAFS) spectroscopy is known to be a valuable tool to probe the local structure. EXAFS has been effectively used to understand the local structural distortions and the spin state of Co ion in the parent RCoO_3 compounds [17, 18, 19, 20, 21, 22, 23]. In comparison to RCoO_3 , the oxygen cage around Co ion is more distorted in $\text{RBaCo}_2\text{O}_{5+\delta}$ [24, 25]. It is suspected that the deformation of polyhedra modify the hybridization between outer orbits of cation (R,Ba,Co) and $2p$ orbitals of oxygen ion which affect electric and magnetic properties of double perovskites [26]. Furthermore, the difference between the ionic radii of R and Ba along with deformed polyhedra will affect the crystal field splitting of the $3d$ band [27]. Herein we report EXAFS spectroscopy investigations on two oxygen rich $\text{PrBaCo}_2\text{O}_{5+\delta}$, ($\delta = 0.80$ and 0.67) compounds crystallizing in the same 112 type structure but having different magnetic ground states. While FM dominates in compound with $\delta = 0.8$, the other one ($\delta = 0.67$) has predominantly AFM ground state.

2. Experimental

The polycrystalline samples of $\text{PrBaCo}_2\text{O}_{5+\delta}$ were prepared by sol-gel method. Stoichiometric amounts of Pr_6O_{11} , BaCO_3 and $\text{Co}(\text{NO}_2)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in nitric acid. Citric acid was added to the above solution as a complexing agent. The solution was then heated at 353K to form a gel which was subsequently dried at 433K to remove the solvent. This precursor was ground, pelletized and heated at 1073K for 4 hours followed by annealing at 1323 K for 24 hours and slow cooling at the rate of $1^\circ/\text{min}$ to room temperature to get the required sample. This as synthesized sample had an oxygen stoichiometry of $\delta = 0.80 \pm 0.01$ as determined by iodometric titration [28]. To obtain a sample with lower oxygen content, the above as prepared sample was further annealed in Argon atmosphere at 673K for 36 hours and quenched in ice water. The oxygen content as determined by iodometric titration was found to be $\delta = 0.67 \pm 0.01$. X-ray diffraction (XRD) data were recorded using Rigaku D-Max IIC X-ray diffractometer in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with Cu K_α radiation to ascertain phase formation. The diffraction patterns were Rietveld refined using FULLPROF suite and structural parameters were obtained. Resistivity measurements were performed in the temperature range 325K-10K using four probe method. Magnetization measurements were carried out as a function of temperature using a Quantum Design SQUID magnetometer in an applied field of 1000Oe and in the temperature range of 10K to 300K. The sample was initially cooled from room temperature to the lowest temperature (10K) in zero applied field. Magnetization was recorded while warming under an applied field (zero-field cooled (ZFC)) and subsequent cooling (field-cooled cooling (FCC)) and warming (field-cooled warming (FCW)) cycles. The magnetotransport studies were carried out

in longitudinal geometry using OXFORD Spectromag 10T magnet. Resistance as a function of temperature $R(T)$ was measured in the range 10K - 300K in 0T and 8T during warming and cooling cycles. Isothermal magneto-resistance MR was measured at selected temperatures by ramping the field in the range $\pm 8T$. The local structure around Co ion was investigated by measuring X-ray absorption fine structure (XAFS) at the Co K edge at various temperatures between 325K to 20K. These experiments were carried out in transmission using BL 7C at Photon Factory Japan. The absorbers were prepared by sprinkling finely powdered sample on a scotch tape and stacking such layers to obtain optimum thickness such that $\Delta\mu t < 1$.

3. Results

Rietveld refinement of room temperature XRD patterns of $\text{PrBaCo}_2\text{O}_{5+\delta}$ for $\delta = 0.67$ and 0.80 confirm the formation of single phase samples with 112 type tetragonal unit cell belonging to $P4/mmm$ space group. As can be seen from Figure 1 both compounds show presence of very minor impurity phases ($\sim 1\%$) with peaks around $2\theta \sim 29^\circ$ and 31° which can be ascribed to unreacted Pr-oxides (Pr_2O_3 , Pr_6O_{11}). The lattice parameters obtained from Rietveld refinement are given in Table 1. The parameters obtained are in good agreement with the neutron diffraction results on $\text{PrBaCo}_2\text{O}_{5.75}$ [11, 13]. However, high resolution synchrotron XRD measurements on similar composition reveal that the structure belongs to orthorhombic unit cell with $Pmmm$ space group [29]. In the present case no splitting of (200) reflection as expected for an orthorhombic structure was seen. It must be noted here that a structural crossover from tetragonal to orthorhombic unit cell is reported for oxygen concentration around $\delta = 0.6$. [11, 16].

Table 1. Lattice parameters for $\text{PrBaCo}_2\text{O}_{5+\delta}$.

δ	a(Å)	b(Å)	c(Å)	V(Å ³)
0.80	3.9045(1)	3.9045(1)	7.6355(2)	116.410(7)
0.67	3.9085(7)	3.9085(7)	7.6311(2)	116.579(5)

Temperature dependant magnetization $M(T)$ measured at 1000 Oe during ZFC, FCC and FCW cycles for the two samples is presented in Figure 2. In case of $\delta = 0.80$, a clear PM to FM transition can be seen at $T_C = 147K$. The bifurcation seen between ZFC and FC curves at lower temperatures ($T \sim 120K$) indicates a presence of competing magnetic interactions. The general behaviour of magnetization is similar to that reported for $\text{PrBaCo}_2\text{O}_{5.75}$ [13].

In case of $\delta = 0.67$, a small rise in magnetization, akin to a PM to FM transition is noticed at 150K. However, the small value of magnetic moment and the subsequent sharp decrease in magnetization at $T = 100K$ prompts us to ascribe both these transitions at $T_{N1} = 150K$ and $T_{N2} = 100K$ to an AFM ground state. In $\text{PrBaCo}_2\text{O}_{5.5}$, where magnetization has similar behavior, neutron diffraction studies have reported

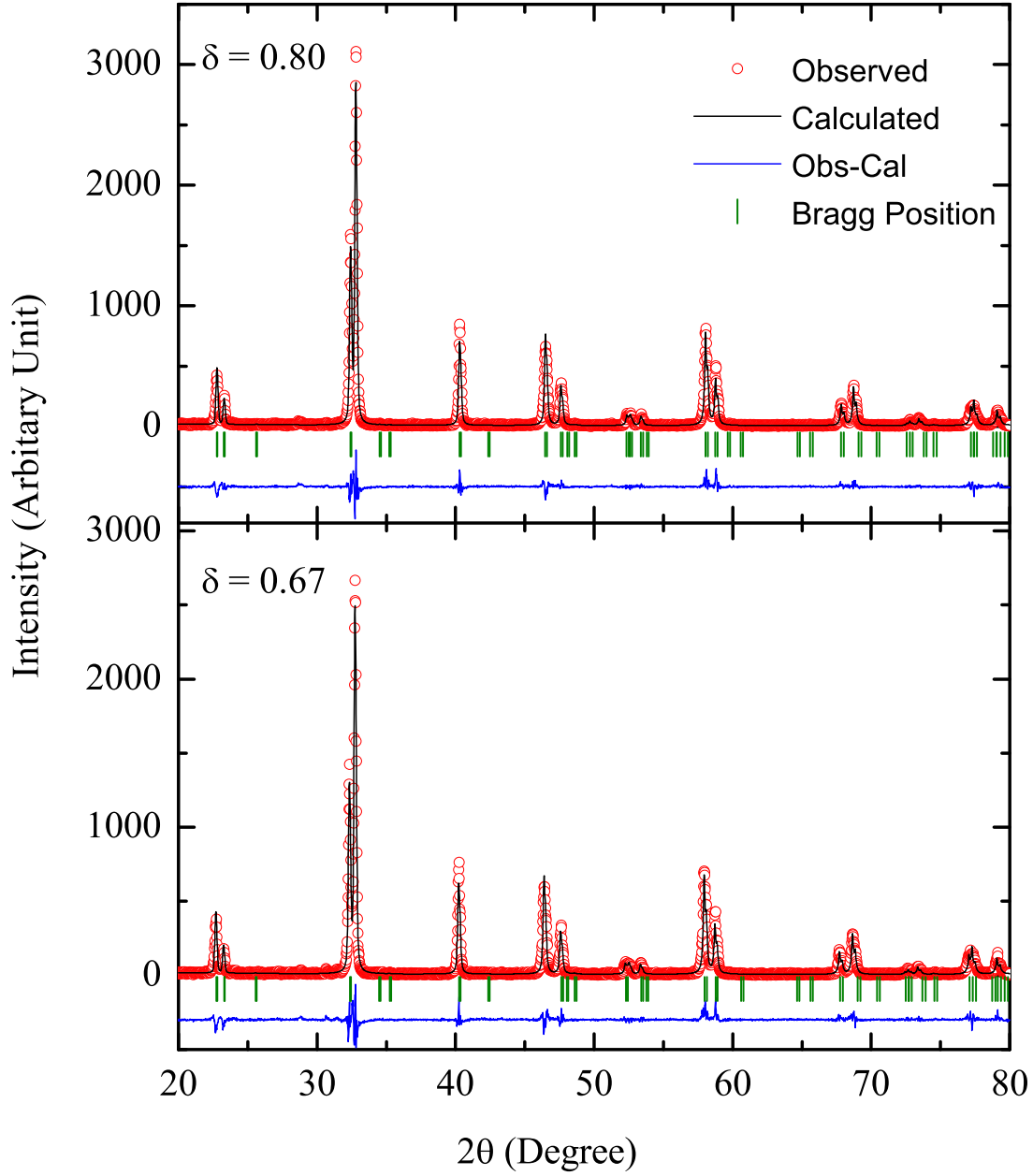


Figure 1. Rietveld refined XRD patterns of $\text{PrBaCo}_2\text{O}_{5.5}$. Circles represent experimental data, continuous line through the data is the fitted curve, vertical lines indicate Bragg positions and the difference pattern is shown at the bottom as solid line.

antiferromagnetic spin alignment [14].

One more transition, T_{R1} is observed at 50K and 37K for $\delta = 0.80$ and $\delta = 0.67$ respectively which are more clearly shown in Ref. [16] and indicated by arrows in Fig. 2. In literature these have been attributed to reorientation of magnetic ordering due to structural transition [27].

Magnetic susceptibility $\chi = M/H$ calculated from magnetization also reveals important clues about magnetic ordering in these two compounds. In the case of $\text{PrBaCo}_2\text{O}_{5.80}$, a plot of χ^{-1} vs T exhibits a Curie-Weiss (linear) behavior almost down to its T_C . The values of paramagnetic Curie temperature, θ_p and effective magnetic moment μ_{eff} are 150K and $5.34 \mu_B/f.u.$ respectively and are in good agreement with those reported for $\text{PrBaCo}_2\text{O}_{5.75}$ [13].

Deviation from Curie-Weiss fit are noted at temperature as high as 250K in case of $\text{PrBaCo}_2\text{O}_{5.67}$. The deviation and the behavior of susceptibility can be ascribed to presence of weak antiferromagnetic correlations well above its ordering temperature. Though θ_p obtained from Curie-Weiss fit is positive, there is a decrease in its value from 150K for $\delta = 0.80$ to 92K for $\delta = 0.67$. Canting of magnetic spins due to different local environment of Co ions and/or their spin states could be the reason for positive values of θ_p . Neutron diffraction studies have indicated AFM ordering at $T_N = 220\text{K}$ in $\text{PrBaCo}_2\text{O}_{5.5}$ [14]. This ordering is a result of interaction between IS Co^{3+} ions in square pyramidal coordination. A possibility $\text{Co}^{3+} - \text{O} - \text{Co}^{3+}$ pairs giving rise to weak antiferromagnetic correlations in $\text{PrBaCo}_2\text{O}_{5.67}$, well above its magnetic ordering temperature cannot be ruled out. The value of μ_{eff} obtained from Curie-Weiss fit is $5.41\mu_B/f.u.$

Based on the similarities of μ_{eff} values and their agreement with that of reported for $\text{PrBaCo}_2\text{O}_{5.75}$ prompts us to assign LS state for Co^{4+} ions and HS/IS state for Co^{3+} . It may be also noted that a simple calculation of magnetic moment of Co ions assuming all Co^{4+} to be in LS state and octahedral Co^{3+} ions in HS while square pyramidal Co^{3+} in IS state gives a value of $5.47\mu_B/f.u.$ which is in good agreement with that obtained from Curie Weiss fit. With a decrease in δ , the concentration of Co^{3+} ions will increase giving rise to a higher possibility of $\text{Co}^{3+} - \text{O} - \text{Co}^{3+}$ pairs. Clusters of square pyramidal Co^{3+} ions can influence antiferromagnetic interactions at higher temperatures.

Electrical resistivity exhibits semiconducting behavior with negligible hysteresis in the entire temperature range (10K - 330K) for the two compounds, $\delta = 0.8$ and 0.67 (Figure 3(a)). A comparison of resistivity curves shows that resistivity as well as the change in resistivity are much higher for $\text{PrBaCo}_2\text{O}_{5.67}$. For $\delta = 0.67$, the resistance changes by almost 5 orders of magnitude from $\sim 10^{-1}\text{Ohm-cm}$ at 300K to $\sim 5 \times 10^3\text{Ohm-cm}$ at 25K while in case of $\delta = 0.8$, it changes from $\sim 10^{-3}\text{ Ohm-cm}$ to 10^{-1} Ohm-cm in $300\text{K} \geq T \geq 25\text{K}$. A plot of $\ln \rho$ v/s $T^{-1/4}$ presented in Figure 3(b) and (c) exhibits a linear variation for a large temperature range indicating variable range hopping (VRH) to be the dominant mechanism of conduction in both the compounds. However, the hopping temperature is much higher for $\delta = 0.67$ as compared to that in $\delta = 0.8$.

Isothermal magnetoresistance (MR) for $\text{PrBaCo}_2\text{O}_{5.8}$ measured at various

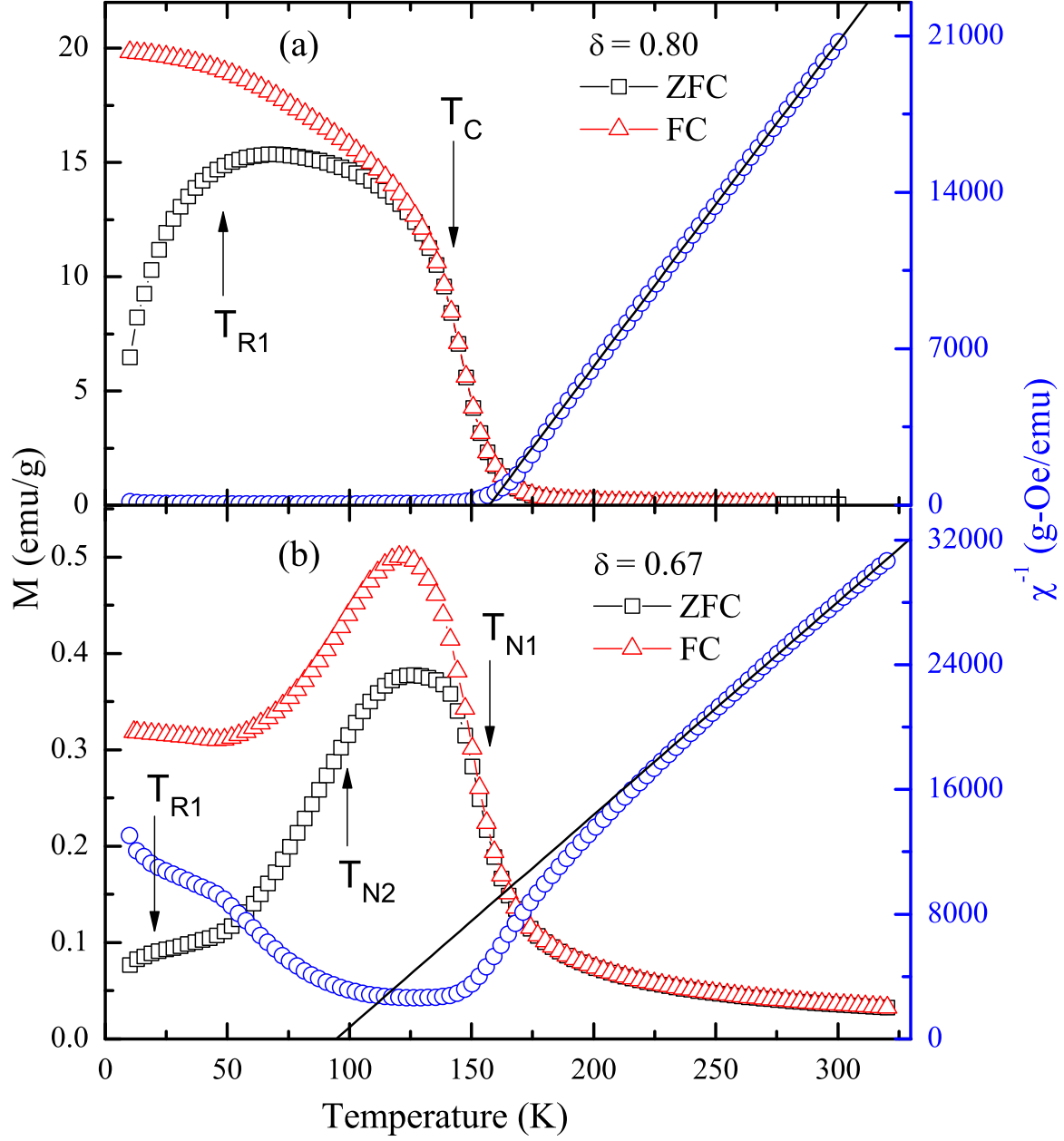


Figure 2. Temperature dependent magnetization $M(T)$ in the field of 1000 Oe for ZFC and FC cycle indicated by open squares and triangles respectively. The magnetic transitions are indicated by arrows. $1/\chi$ Vs Temperature is denoted by circles along with Curie-Weiss fit indicated by solid line. (a) $\delta = 0.80$ (b) $\delta = 0.67$

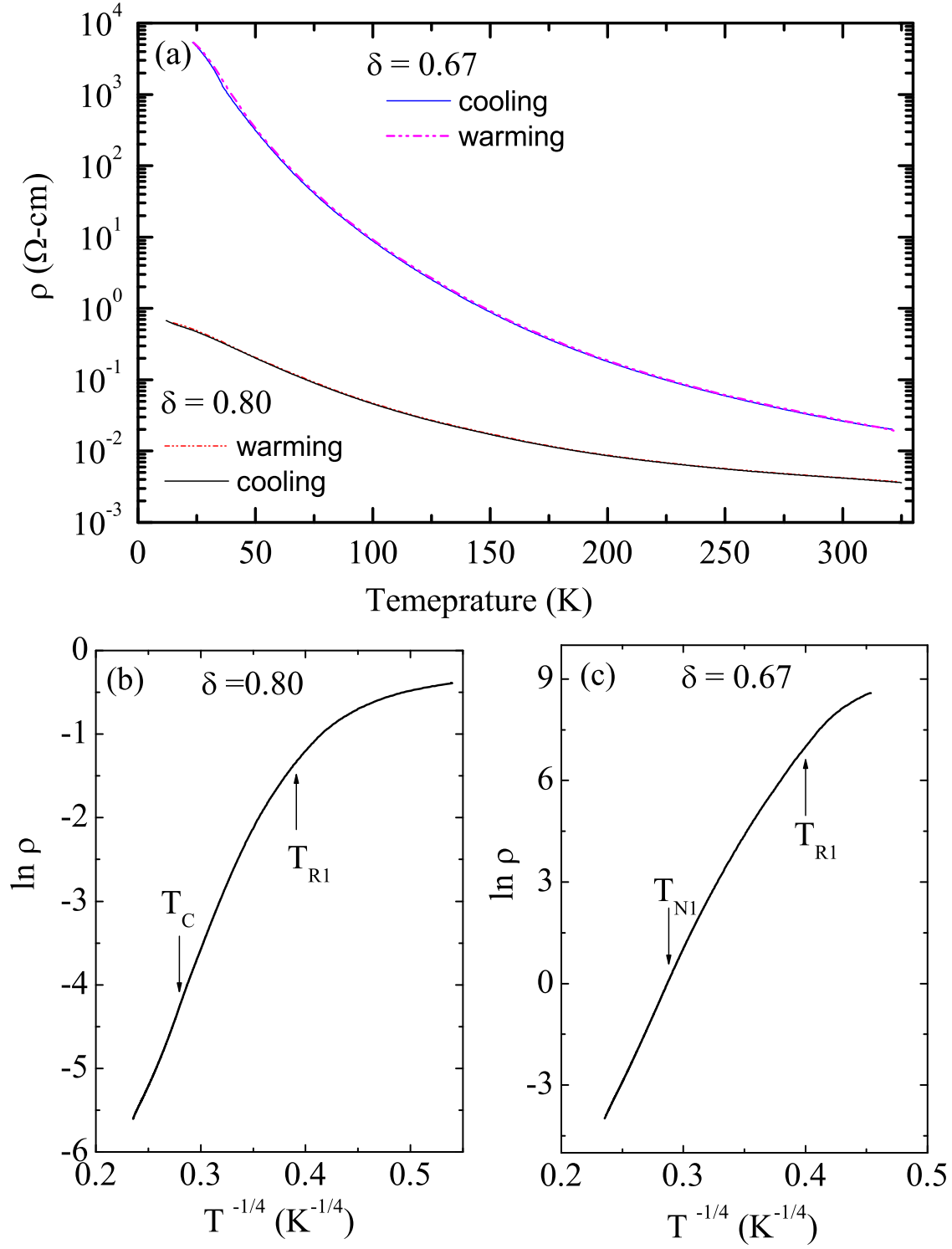


Figure 3. (a) Plot of resistivity with temperature during cooling and warming cycles. (b) Logarithm of the resistivity versus $T^{-1/4}$ plot with arrows indicating different transitions.

temperatures in the field range of ± 8 T are shown in Figure 4. MR is quite large ($\sim 40\%$ at 10K and 8T) and negative at $T \leq 100$ K as expected for a ferromagnetically ordered sample. An interesting feature to be noted is the irreversibility of MR measured while ramping the magnetic field in both directions. This irreversibility of MR gives rise to "butterfly-like" pattern below 50K. Normally such an effect is observed near magnetic phase boundary or due to presence of competing magnetic interactions [8]. This observation augers well with the observation of T_{R1} at 50K in $\text{PrBaCo}_2\text{O}_{5.8}$. It may be also noted that hysteresis recorded at 5K and in the field of ± 14 T fails to show saturation of magnetic moment [16]. Hence even though the compound shows bulk ferromagnetic character below its T_C , there could be weak competing magnetic interactions present due to minority Co^{3+} -O- Co^{3+} pairs.

In the case of $\delta = 0.67$ MR is negative but small ($\sim 3\%$ at 8T) and for $T \leq 50$ K, exhibits positive values at low fields (see Figure 5). The positive values of MR indicate antiferromagnetic ground state. However, the crossover to negative values at low fields and butterfly-like effect hints at presence of competing magnetic interactions or even field induced magnetization. This is in general agreement with inferences drawn from magnetization results which show presence of antiferromagnetic correlations at higher temperatures as well as large difference in ZFC and FC values at low temperatures. Attempts were made to measure MR at higher temperatures but no specific trend could be made out as the values were very small.

The presence of competing magnetic interactions, presence of short range correlations at temperatures much above ordering temperature, irreversibility in isothermal magnetoresistance make it evidently clear that the local structure around Co and its spin state play an important role in governing magnetic and transport properties of these layered double perovskites. EXAFS measurements at Co K edge and at various temperatures can give an insight of changes in local structure and spin state of Co ions. The temperature dependant EXAFS spectra recorded at various temperatures were treated using IFEFFIT software [30]. The absorption data was first processed using Athena to extract the EXAFS signal $\chi(k)$ from μ v/s E data [31]. The $\chi(k)$ v/s k data was Fourier transformed (FT) and fitted with theoretically calculated EXAFS signal for the known crystal structure in Artemis [32]. The theoretical standards were calculated using FEFF 6.01 [33] and lattice parameters from Table 1. Figure 6 (a) and (d) presents magnitude of FT of k^3 weighted $\chi(k)$ data for the two compounds $\delta = 0.8$ and 0.67 respectively. EXAFS spectra in the range 1-4 Å were fitted with Co-O, Co-Co and Co-Pr/Ba single scattering and Co-O-Co multiple scattering correlations. The fitting parameters were defined using relations based on lattice parameters to reduce interdependency and number of variables. The solid lines in Figure 6 (a) and (d) respectively depict the best fit obtained to experimental data at 20K. The variations of Co-O bond distances and Co-O-Co bond angle obtained from fitting are presented in Figure 6 (b) and (c) for $\delta = 0.80$ and (e) and (f) for $\delta = 0.67$ respectively.

In the case of $\delta = 0.8$, it can be seen that the Co-O planar bond length (Figure 6(b)) decreases steadily with temperature followed by an increase around 150K which

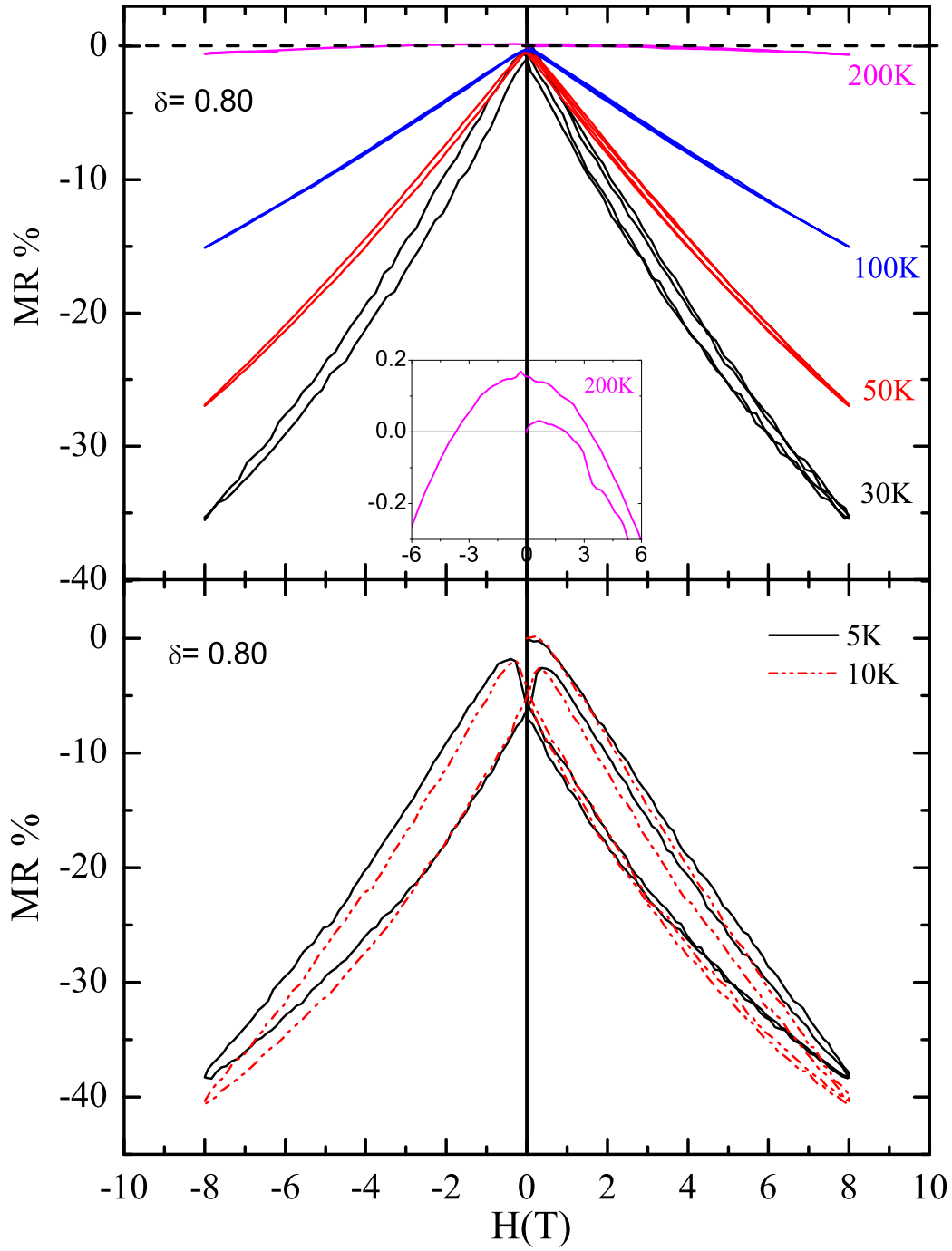


Figure 4. Magnetic-field-dependent isothermal magnetoresistance at various temperatures for $\delta = 0.80$. Inset shows enlarge view of positive going MR at 200K.

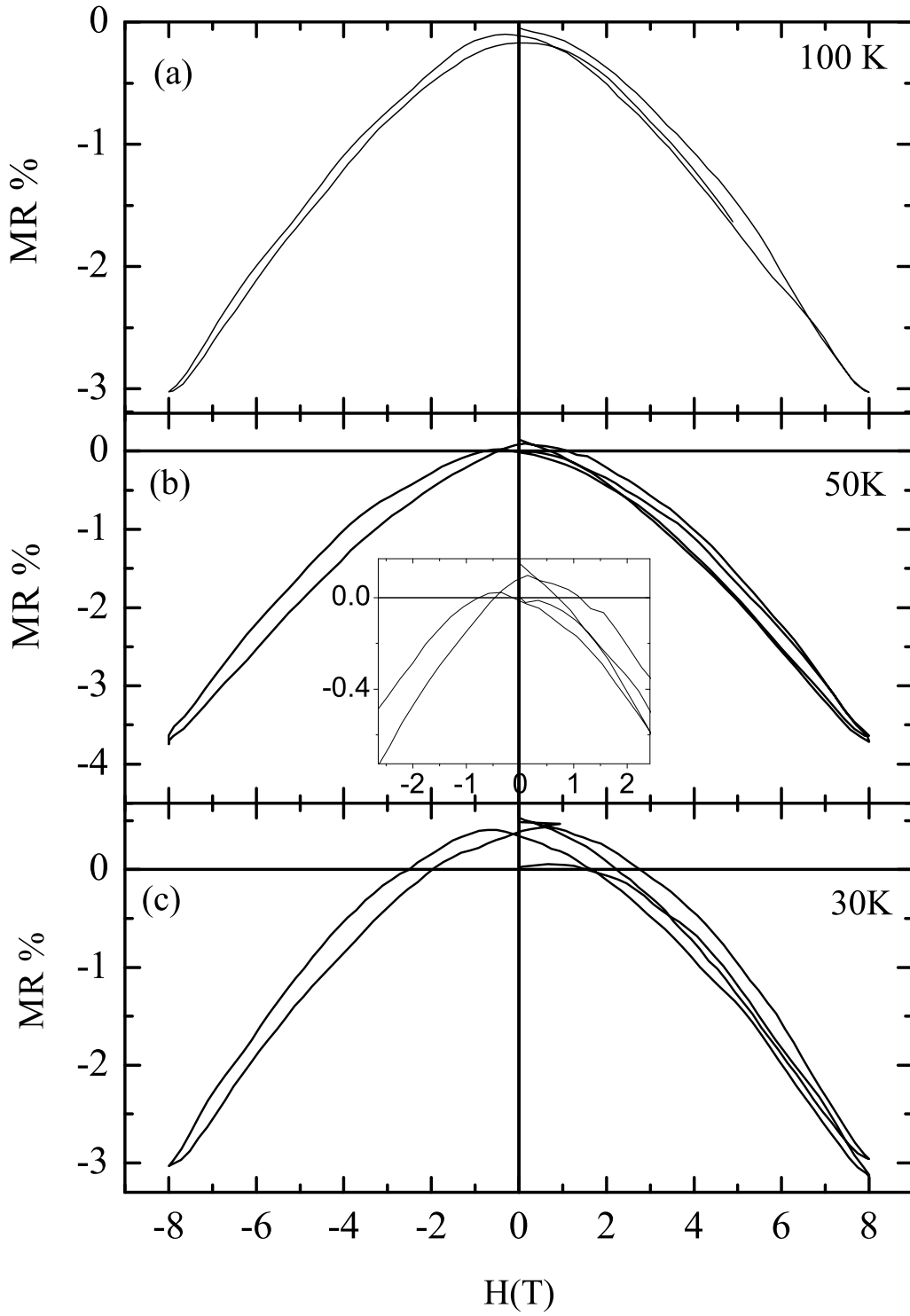


Figure 5. Magnetic-field-dependent isothermal magnetoresistance at various temperatures for $\delta = 0.67$, (a) 100K, (b) 50K; Inset shows enlarged view of positive going MR at 50K, (c) 30K.

coincides with the T_C of the compound. A similar behavior is also noted for the planar Co-O-Co bond angle (Figure 6(c)). On the other hand, the Co-O apical bond distance exhibits a step like behavior with an increase around 240K. This elongation of CoO polyhedra along c -axis and the concomitant shrinkage in Co-O planar bond length and the Co-O-Co bond angle corresponds to the tilting of CoO polyhedra towards each other. Further, at lower temperatures (~ 150 K) the polyhedra rotate about c axis resulting in increase of Co-O planar bond length and the planar Co-O-Co bond angle.

A similar variation of bond distances can be seen in the case of $\delta = 0.67$. The elongation along c -axis and tilting of Co-O polyhedra can be seen to happen around 300K (Figure 6(e), (f)). At lower temperatures, the apical Co-O bond distance is found to remain nearly constant while the planar Co-O bond distance and Co-O-Co bond angle exhibit identical variation with temperature. In particular, the planar Co-O bond distance and bond angle show two minima centred at about 250K and 100K and a maxima at around 150K. Interestingly these temperatures respectively correspond to onset of magnetic correlations as seen from Curie-Weiss analysis of susceptibility, and the antiferromagnetic ordering temperatures, T_{N1} and T_{N2} of the compound.

4. Discussion

The two compounds under study $\text{PrBaCo}_2\text{O}_{5+\delta}$ with $\delta = 0.67$ and 0.80 crystallize in tetragonal unit cell with $P4/mmm$ structure. However, they exhibit contrasting magnetic behavior. While $\text{PrBaCo}_2\text{O}_{5.8}$ orders ferromagnetically below 147K, $\text{PrBaCo}_2\text{O}_{5.67}$ has an antiferromagnetic ground state. In the case of $\text{PrBaCo}_2\text{O}_{5.80}$, charge balance demands 30% Co ions to be in tetravalent state while the rest 70% to be in trivalent state. The value of μ_{eff} obtained from Curie-Weiss analysis of susceptibility and its agreement with that reported for $\text{PrBaCo}_2\text{O}_{5.75}$ [13] indicates that Co^{4+} ion are in LS state while Co^{3+} ions are in HS/IS state. Therefore the observed FM ordering can be ascribed to double exchange (DE) interaction between LS Co^{4+} (t_{2g}^5, e_g^0) and HS/IS Co^{3+} (t_{2g}^5, e_g^1 or t_{2g}^4, e_g^2) ions. These DE interactions are facilitated by tilting and the rotation of Co^{3+}O and Co^{4+}O polyhedra towards each other about the c axis. This increases the Co(3d) - O(2p) hybridization leading to a ferromagnetic order. The change in hybridization also promotes hopping conduction behavior resulting in lower values of resistivity. Mott's VRH law is best obeyed in the temperature region between 200K and 50K. Deviations from linearity can be noticed below and above this temperature range. MR also exhibits irreversibility at $T \leq 50$ K and positive values at low fields at $T = 200$ K. It may be noted that $T = 200$ K corresponds approximately to the temperature at which Co-O polyhedra tilt towards each other while the weak AFM interactions noticed below 50K could be implied to be due to superexchange (SE) interactions between Co^{3+} ions as per Goodenough-Kanamori rule.

For $\text{PrBaCo}_2\text{O}_{5.67}$, the properties are found to be very different. With the decrease in oxygen content though the percentage of Co in square pyramidal coordination and those in trivalent state increases the value of μ_{eff} obtained from Curie Weiss

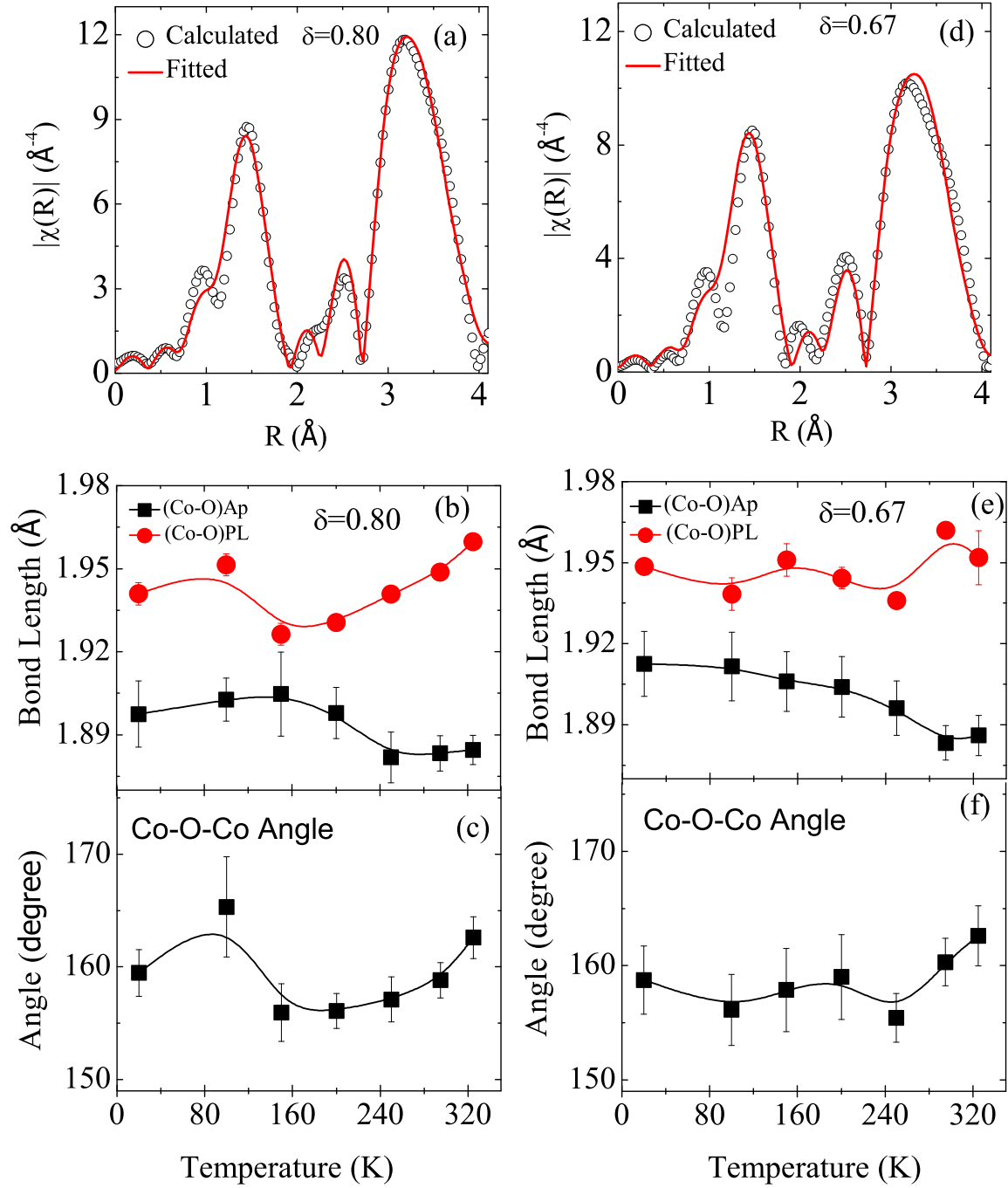


Figure 6. (a) and (d) EXAFS $\chi(k)$ data and best fit, (b) and (e) variation of average Co-O bond distances Planer and Apical (c) and (f) Co-O-Co bond angle at various temperatures for PrBaCo₂O_{5.80} and PrBaCo₂O_{5.67} respectively.

fit to susceptibility is nearly the same as that in $\text{PrBaCo}_2\text{O}_{5.80}$. This implies that Co^{3+} continue to be in HS/IS state and the Co^{4+} ions in LS state. Therefore antiferromagnetic superexchange interaction can be expected between neighboring CoO polyhedra containing trivalent cobalt ions while the Co^{3+} -O- Co^{4+} pairs will interact via double exchange mechanism. EXAFS studies indicate that the antiferromagnetic SE interactions are a result of the outward rotation of Co^{3+}O polyhedra about the c -axis. The presence of competing ferromagnetic interactions arising due to DE interactions can give rise to canting of Co spins resulting in an increase in magnetization at about 150K. The antiferromagnetic order localizes the charge carriers leading to a much higher resistivity as compared to $\delta = 0.8$ compound and a much lower MR even near the AFM transition.

5. Conclusion

In summary, it can be concluded that the local structure and the changes therein play an important role for magnetic and transport properties of layered perovskites. In the case of $\delta = 0.80$ the inward rotation and tilting of the neighboring Co^{3+}O and Co^{4+}O polyhedra about the c -axis facilitates DE mechanism between LS Co^{4+} and HS/IS Co^{3+} ions leading to ferromagnetic order. While in case of $\delta = 0.67$ the tilting and outward rotation of the neighboring Co^{3+}O polyhedra away from each other supports Co^{3+} - O- Co^{3+} superexchange mediated antiferromagnetic ordering.

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